COATINGS. ENAMELS

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SILICOPHOSPHATE GLASSES AS A COMPONENT OF BIOACTIVE COATINGS

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The compositions and properties of bioactive silicate materials are considered. Biocompatible sodium-silicophosphate glasses for the formation of coatings over titanium implants are developed and investigated.

The substantial expansion in the range of materials used in restorative surgery, orthopedies, and dentistry that took place in the last 30 years is due to the development of ceramic, glass ceramic, and vitreous materials as volume implants or coatings over metal implants and in the treatment of wounds and diseases.

A whole set of factors influence a biomaterial inside a human body at physiological temperature: salt solutions, organic acids, dissolved oxygen, etc., which create an active corrosive medium, whose effect can be diverse in the case of biomaterials of different compositions.

The sensitivity of a living organism to incorporation of foreign materials, which is manifested in the reaction of rejection, allergy, and other effects, restricts selection of the chemical composition of biomaterials since an implant should be biocompatible with body tissue.

Bioceramics, bioglasses, and bioglass ceramics are the most promising materials, since their synthesis offers a unique possibility of obtaining materials that contain crystalline phases typical of the mineral components of natural bones and the elements present in the living body. The prospects of this class of materials are also determined by the possibility of obtaining bioinert, bioactive, and biodegradable materials.

Various minerals and elements are present in human tissues and organs (Table 1) [1].

About 30 vol.% of bone tissue is represented by an organic substance, of which 90 – 95% is collagen containing silicon; 10% of the tissue is constituted by water in the free and fixed states. Around 60% of bone issue is represented by hydroxyapatite, which is not found in biological systems in the stoichiometric state. Biological apatite is usually regarded as deficient in calcium, nonstoichiometric, or carbonate-containing and exists in the insoluble crystalline form (to a greater extent) and in the form of colloid solutions, which can be described by the formula $Ca_{10}(PO_4)_6(OH)_2 \cdot ([Ca_3(PO_4)_2]_3 \cdot [Ca(OH)_2])$. Amorphous calcium phosphates are believed to be the precursors of hydroxyapatite in the complicated sequence of transformations, and they, in turn, are formed in the accumulation of calcium ions in the intercellular space of the bone matrix.

The mineral component of natural bone, beside the crystalline and amorphous calcium phosphates, also contains (wt.%): 5.90 $CaCO_3$, 0.72 MgO, 0.99 Na_2O, 0.07 K_2O, 0.04 SiO_2, 3.48 CO_2, 0.07 F, 0.08 Cl.

TABLE 1

Calcium compounds	Chemical formula	Ca : P ratio
Amorphous calcium phosphate	$(Ca, Mg)_m \cdot (PO_4, Y)_n$	–
Dicalcium phosphate dihydrate, brushite	$CaHPO_4 \cdot 2H_2O$	1.00
Dicalcium phosphate, monetite	$CaHPO_4$	1.00
Octacalcium phosphate	$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	1.33
Tricalcium phosphate, β-TCP, whitlokite	$Ca_3(PO_4)_2$	1.50
Magnesium-substituted whitlokite	$(Ca, Mg)_3(PO_4)_2$	1.50
Calcium pyrophosphate dihydrate	$Ca_2P_2O_7 \cdot 2H_2O$	–
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	1.67
Apatite	$(Ca, Z)_{10}(PO_4, Y)_6(OH, X)_2$	1.67
Fluorite	CaF_2	–
Calcite	$CaCO_3$	–

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Natural bone includes several microelements, the most important of which are Cu, Zn, Sr, Ba, Be, Al, Mo, Au, Mn, Fe, and Si. It is believed that a shortage or an excess in the content of these elements may have a determining role in the renewal of the crystalline lattice of the bone minerals and determines its spatial structure, which to a large extent is responsible for the strength parameters of bone tissue.

Thus, calcium-phosphates minerals exist in the body not as individual phases but as a dynamic system, in which an intense mineral exchange proceeds under the effect of physiological factors. Bone tissue is not only a depot, but also a buffer system maintaining a constant concentration of calcium and phosphorus ions in blood and in the body. This is a complex structure, which should be taken into account in developing biomaterials that should have a positive effect on all organizational levels of bone tissue, starting with the mineral components, to biopolymers, proteins, and ending with osteogenic cells. Such approach appears the most rational, since it is oriented to the development of an integrated implant – bone functional system [1].

The understanding of the general regularities of mineral exchange in a living organism and the experience accumulated in model experiments contributed to the formation of the main principle in developing highly compatible bioactive materials, i.e., artificial reproduction of the chemical and phase compositions of the mineral component of natural bone. The extensive research in the development of bioactive ceramics and glass ceramics in Russia and abroad is mainly directed to the production of multiphase polycrystalline materials, whose main phases are calcium phosphates, and which also contain calcium silicates: wollastonite, anorthite, and diopside to ensure the required mechanical properties.

Analyzing the results of studying the bioactivity of silicophosphate glasses, K. Karlson [2] convincingly showed that bioactive glass, including glass which is present in polyphase materials facilitates the formation of bone tissue. With a silica content below 55 wt.%, the silicate substructure is mostly represented by single and dual silicon-oxygen tetrahedra. In leaching of glass they form a permeable gel, over which and inside which a hydroxyapatite layer is formed, which is required for further nucleative formation of mineral layers. The bone cells become attached to hydroxyapatite as its structure grows more ordered. It is believed that bioactive glasses, i.e., those capable of intergrowth with living bone tissue, can only be glasses that contain alkaline oxides in an amount sufficient to form silica gel in leaching, which is the basis for the nucleation of hydroxyapatite crystals.

The formation of a new bone firmly fixing the implant to the live bone is named osteo-integration. The ingrowth of the implant with the bone in the framework of the bioactivity concept is accomplished when the synthetic material, as a consequence of biodegrading, releases biologically active ions into the surrounding medium, primarily calcium ions and phosphate ions, which are used by the organism to form a layer of biological apatite on the surface of the implant, which then grows together with the live tissue.

It is reported in [3] that silicon, in addition to calcium, has an important role in initiating the crystallization process. Leaching of silicon from glass ceramics leads to the formation of hydrated silicate, creating beneficial sites for the formation of apatite nuclei. At the same time, in addition to the physiological factors that accelerate or inhibit the growth of apatite, fluorine ions accelerate and aluminum, magnesium, tin, and carbonate ions inhibit this process [4].

Owing to the increased concentration of calcium and accompanying factors, the process of formation of hydroxyapatite crystal around the implant (osteoinduction) is started. The emergence of new bone tissue and its growth (osteoconduction) on the implant surface becomes possible when a substantial surface area of the contact is provided between the biological liquid and the implant, i.e., with a sufficient (at least 30%) porosity of the latter. It is demonstrated [5] that the size of pores in the material should approach the size of osteons, i.e., structural-functional units of natural bone, i.e., $80 – 300$ μm. When the pore sizes are below 80 μm, osteoinductive properties are not manifested, and with a pore size above 300 μm, osteoconductive properties are significantly impaired [1]. This has a great significance for implants fulfilling the function of bone substitution for the purpose of ensuring a rapid and strong bond with the live bone.

Although ceramics based on calcium phosphate are undoubtedly effective as implants, their application is restricted by their relatively low mechanical characteristics: brittleness, low tensile and impact strength.

Starting in 1990s, orthopedics and stomatology started using implants made of titanium and titanium alloys coated with hydroxyapatite. The combination of the strength properties of the metal and bioactive properties of the coating material, whose chemical composition correlates with the natural bone metabolites, has opened new opportunities for making diverse implants. The bioactivity concept that was developed for volume implants is also applied to interpret the functions of a coating on a metal implant. It is assumed that quick ingrowth with bone occurs due to partial dissolution of the ceramic layer and subsequent emergence of new hydroxyapatite crystals, which react with collagen and provide for the formation of a normal bone [4].

The process of dissolution (resorption, degrading) of the material is manifested in experiments (*in vitro* and *in vivo*) in different ways; however, it is believed that all coatings containing calcium phosphates on being introduced into bone tissue are subjected to biodegrading with subsequent transformation into bone-like apatite. There are published data on the sequence of dissolution: β-tricalciumphosphate, carbonate-substituted fluorhydroxyapatite, and calcium-deficient fluorhydroxyapatite [1]. In biphase ceramics whitlokite dissolves first, and hydroxyapatite afterward.

Hydroxyapatite coatings over titanium and alloys based on synthetic or natural materials are of chief practical interest. Methods of applying coating may differ: plasma spray-

ing, electrochemical precipitation, slip casting of coating, fixation using a vitreous binder, etc.

In contrast to bioinert coatings based on titanium oxides that provide for mechanical fixation of an implant to bone, coatings containing calcium phosphates and, in particular, hydroxyapatite, provide for biological fixation.

In spite of the first successes in practical application of such implants, certain problems persist, the solution of which would ensure the reliability and extent of using this method of implanting. These problems include an insufficient strength of adhesion of coatings to the metal base, the difficulty of controlling the thickness, porosity, and the degree of crystallization of the coating, which determines the extent and rate of degrading in biological medium, and the reliability of the implant fixation.

The possibility of producing hydroxyapatite coatings on titanium using glasses of the $Na_2O - SiO_2 - P_2O_5$ system was investigated taking into account the recent results of studying bioactivity of glass, ceramics, and glass ceramics. The ceramic phase of coatings consisting mainly of hydroxyapatite was produced on the basis of reactant and natural bone. Glasses of this system in coatings are able to fulfill biochemical and technological functions.

The biochemical functions include: ensuring biocompatibility, initiation of the dissolution of the coating by leaching and release of the glass components into the biological medium, and development of conditions for the nucleation of hydroxyapatite crystals due to the formation of silica gel on the coating surface. The technological functions consist in agglomeration of hydroxyapatite particles and in the fixation of hydroxyapatite to the surface of the metal implant.

The experiment used plates of titanium VT-1 and VT-2, which were previously oxidized to improve the adhesion and to guarantee the protection of titanium from diffusion into the biological medium. Besides, the presence of a thin (20 μm) film oxide on the surface of titanium partly removes the problem of coordination of the TCLEs of material and coating.

The glass composition is within the limits of (mol.%) $10 - 20$ Na_2O, $20 - 25$ SiO_2, and $55 - 65$ P_2O_5 and is relatively low-melting. On softening within the temperature interval of $430 - 550°C$, they contribute to agglomeration of the ceramic phase particles, and on further heating provide for adhesion to the base. The low melting point is an important factor, since high temperatures can have a negative effect on the crystalline phase (cause inadmissible growth of grains or decomposition of hydroxyapatite into less stable compounds) and on the metal by breaking its microstructure (the limiting temperature of titanium heating is $880°C$) and producing additional oxidation.

To control the surfactant properties and the TCLE, calcium oxide, titanium oxide, and jointly calcium fluoride and titanium oxide were introduced into the main glass mixture in the amount of $8 - 10\%$ instead of P_2O_5.

The glasses were melted from briquetted batches in corundum crucibles, which are the best for melting high-phosphate compositions due to the low solubility of corundum. The effect of the oxides replaced P_2O_5 on the chemical resistance, TCLE, and spreadability of glasses over oxidized titanium surface was investigated.

The density of glasses upon the introduction of the substitution oxides increased by $1.5 - 6.0\%$, the chemical resistance increased on the average by $5 - 7\%$, at the same time the chemical resistance of glasses is within the interval of $15 - 55\%$, and the optimum properties were exhibited by glasses containing TiO_2 and CaF_2, 5% each. The introduction of substitution oxides produces a significant decrease in the TCLE, by $8 - 30\%$ in relation to the reference three-component glasses.

The temperature interval of softening for the considered glasses is rather wide, from 220 to 340°C, which is favorable for wetting the ceramic phase grains and the substrate surface. The starting temperature of spreading over the oxidized titanium surface is around 480°C for all compositions, and the temperature of complete spreading that corresponds to the contact wetting angle of 30° is 860°C. The structural interpretation of the obtained regularities of variation of properties correlates with the existing concepts.

It is known that silicophosphate glasses are characterized by the presence of silicon-oxygen and phosphate anion substructures. Titanium oxide introduced up to 10% is distributed in the silicon-oxygen lattice. According to the data in [6], the major part of titanium ions exist in the form of a solution in the silicon-oxygen glass component in four coordination. The presence of $Si - O - Ti$ bridges determines the increased cohesion of the silicon-oxygen skeleton, which decreases the TCLE and raises the softening point. This was observed in introducing titanium oxide into the reference glass composition.

It is also known that fluoride is capable of forming various anion groups structurally compatible with the phosphate lattice, for instance, the anion CaF_4^{2-}, furthermore, the presence of fluorophosphate groups in minimal concentrations stabilizes the vitreous state. The absence of crystallization in the considered glass powders is confirmation of the fact that calcium fluoride is distributed in the phosphate substructure of glasses and has a positive effect on spreading and adhesion to the oxidized titanium surface.

The coatings were deposited controlling the slip fluidity using the slip technology. Depending on the dispersion of the ceramic phase, the amount of the vitreous binder, and the application method, the resulting coatings were $100 - 400$ μm thick. The coatings had homogenous penetrating porosity, the crystal size was $50 - 150$ μm, and the pore size was comparable with the crystal size.

The components identified in the coating were hydroxyapatite, tricalciumphosphate, and the amorphous phase in substantial quantities, including the phase formed by glass and by the amorphous phase of the ceramic component of the

coating. The coasting structure was homogenous. The macroporosity depends on the granulometric composition of the ceramic phase, and the microporosity depends on the ceramic phase : glass ratio and increases in the course of glass dissolution.

In heat treatment the degree of crystallinity of hydroxyapatite increases due to crystallization of finely dispersed amorphous particles. The adhesion of the coating to the substrate is determined by the diffusion processes on the coating – substrate boundary. Titanium was detected in the coating layer, and phosphor, calcium, sodium, and silicon were found in the compact metal layer.

As the size of grains of the crystalline phase grows and the porosity exceeds 30 – 40%, the strength of adhesion of the coating to the substrate tends to decrease.

The obtained glasses and composites had a strength of adhesion equal to 2 N/mm^2. The biocompatibility testing results were positive.

Thus, sodium-silicophosphate glasses are promising for the formation of hydroxyapatite-based coatings over tita-nium implants, since they provide for biocompatible properties and fixation of coating under an admissible temperature up to 880°C.

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